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THE AIR FORCE RESEARCH LABORATORY
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Theoretical studies of nanocluster formation

26 May 2016

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Aerospace Systems Directorate, RQRP

Air Force Research Laboratory

This briefing contains information up to:

Outline

1. **Introduction**
   - background, technical approach

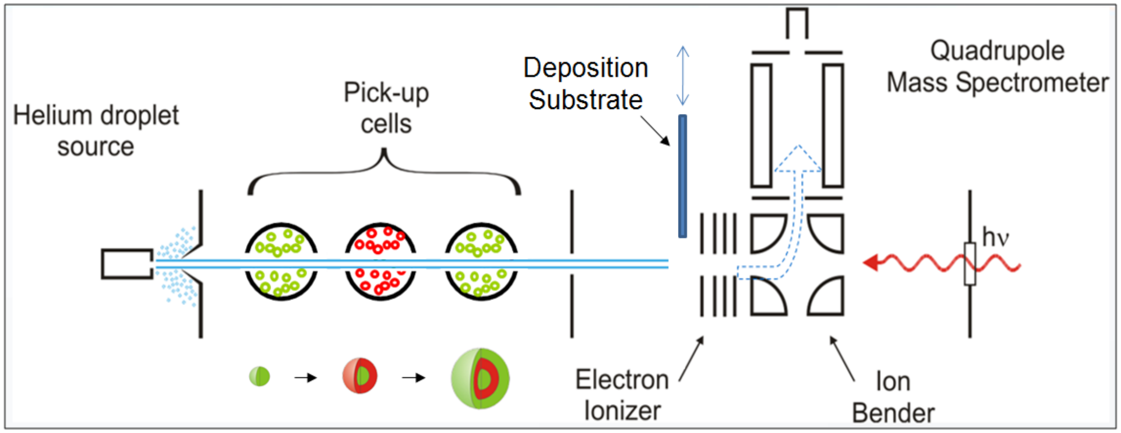
2. **Core-shell nanoclusters (Mg/Cu, Si/Al, etc.)**
   - energetic additives for propellants, explosives
   - gas generators
   - biocidal defeat agents

3. **Summary and conclusions**

Core-shell nanocluster synthesis

Core-shell nanoclusters such as $SiAl_n$, Ni_nAl_m, $Al_n(CuO)_m$, etc. may be useful ingredients in propellants and explosives

- **higher energy densities than organics (~ 3x RDX)**
- **some are resistant to surface oxidation (i.e., “magic clusters”)**



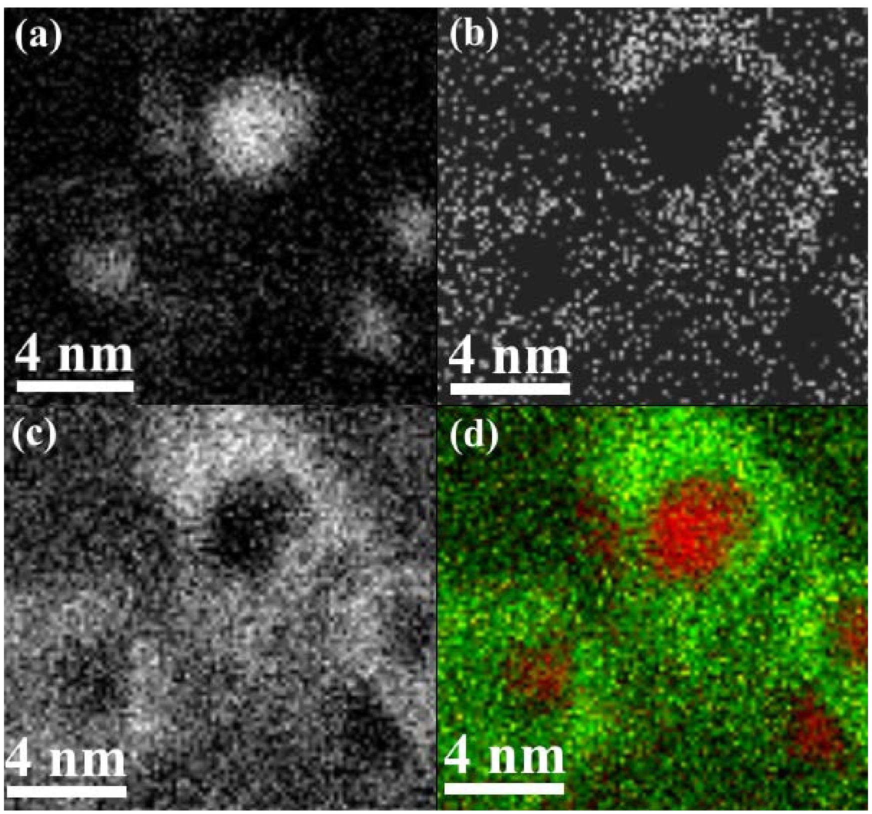
Helium droplet experiments at AFRL/RW

Can core-shell nanoclusters be formed under cryogenic conditions (i.e., in helium droplet experiments) via stepwise condensation; i.e., what are the energy barriers (if any) to stepwise addition of atomic Al?

$$SiAl_n + Al \rightarrow SiAl_{n+1}\ ;\ [Al_n]^- + Al \rightarrow [Al]^-$$

Cu_xMg_y core-shell nanocluster inversion

In helium droplet experiments, Mg atoms were captured in first pickup cell, followed by capture of Cu atoms to form Cu_xMg_y core-shell nanoclusters. However, scanning transmission electron microscopy (STEM) measures show cluster inversion occurred to produce Mg_yCu_x(!)

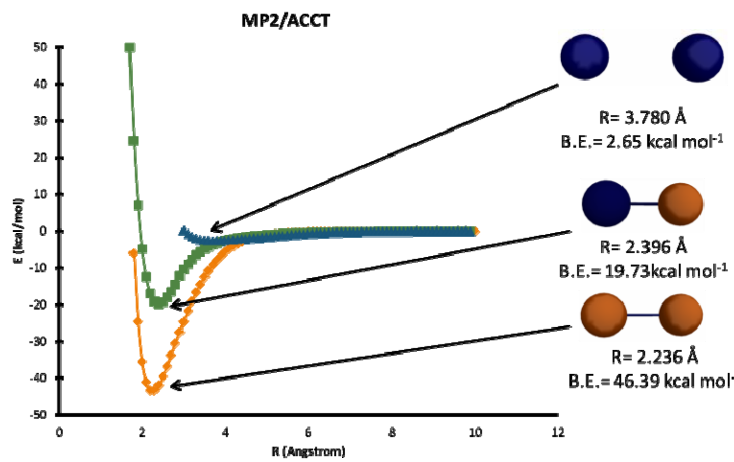


a) copper atoms

b) magnesium atoms

c) oxygen atoms

d) composite image



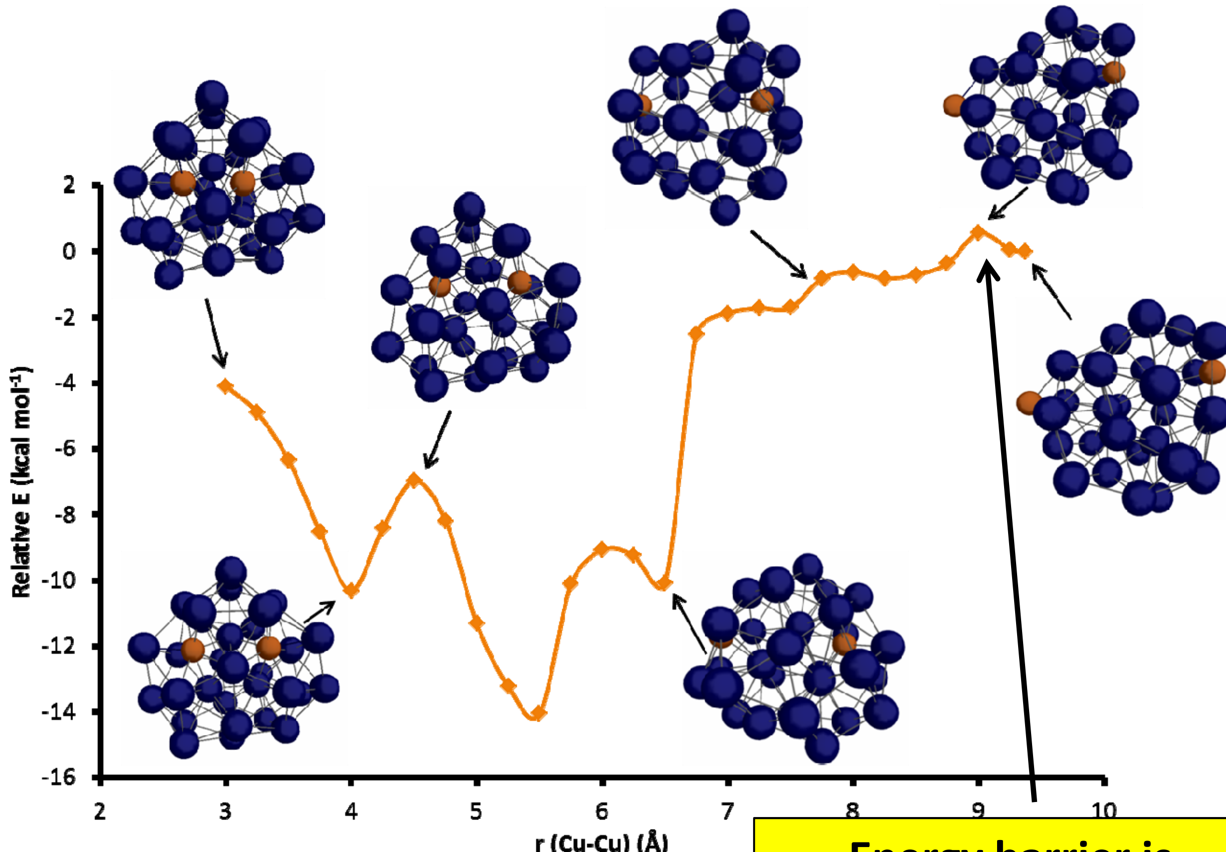
Cu_2Mg_{30}

1. Structure of Mg_{30} cluster was fully optimized.

2. Two Cu atoms were placed on opposite sides of Mg_{30} and structure reoptimized.

3. Distance between Cu atoms was decreased in steps of 0.25 Å, held fixed, and remaining DOF reoptimized.

4. Total energy plotted as function of fixed Cu-Cu distance.

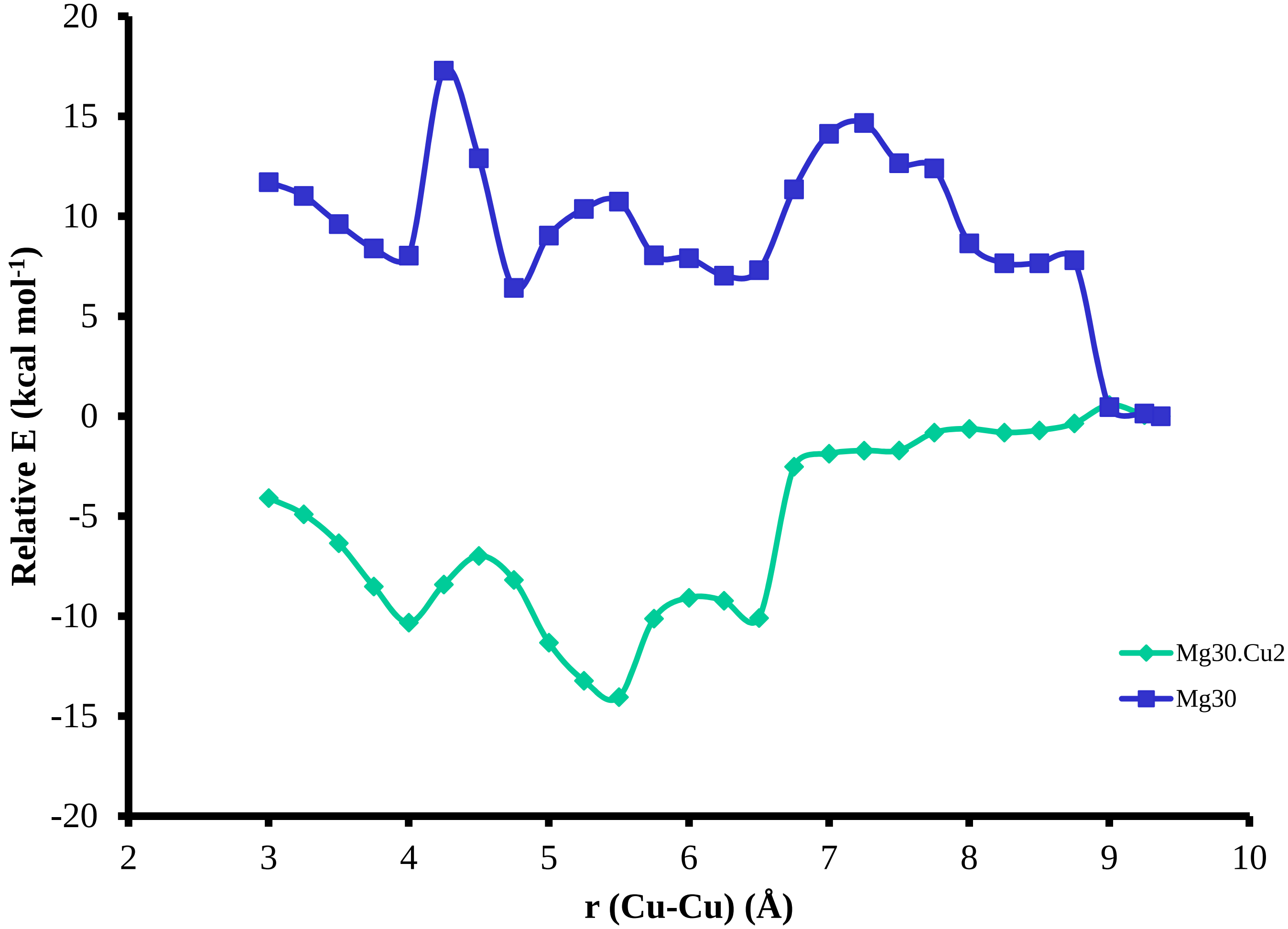


Energy barrier is ~0.5 kcal/mol

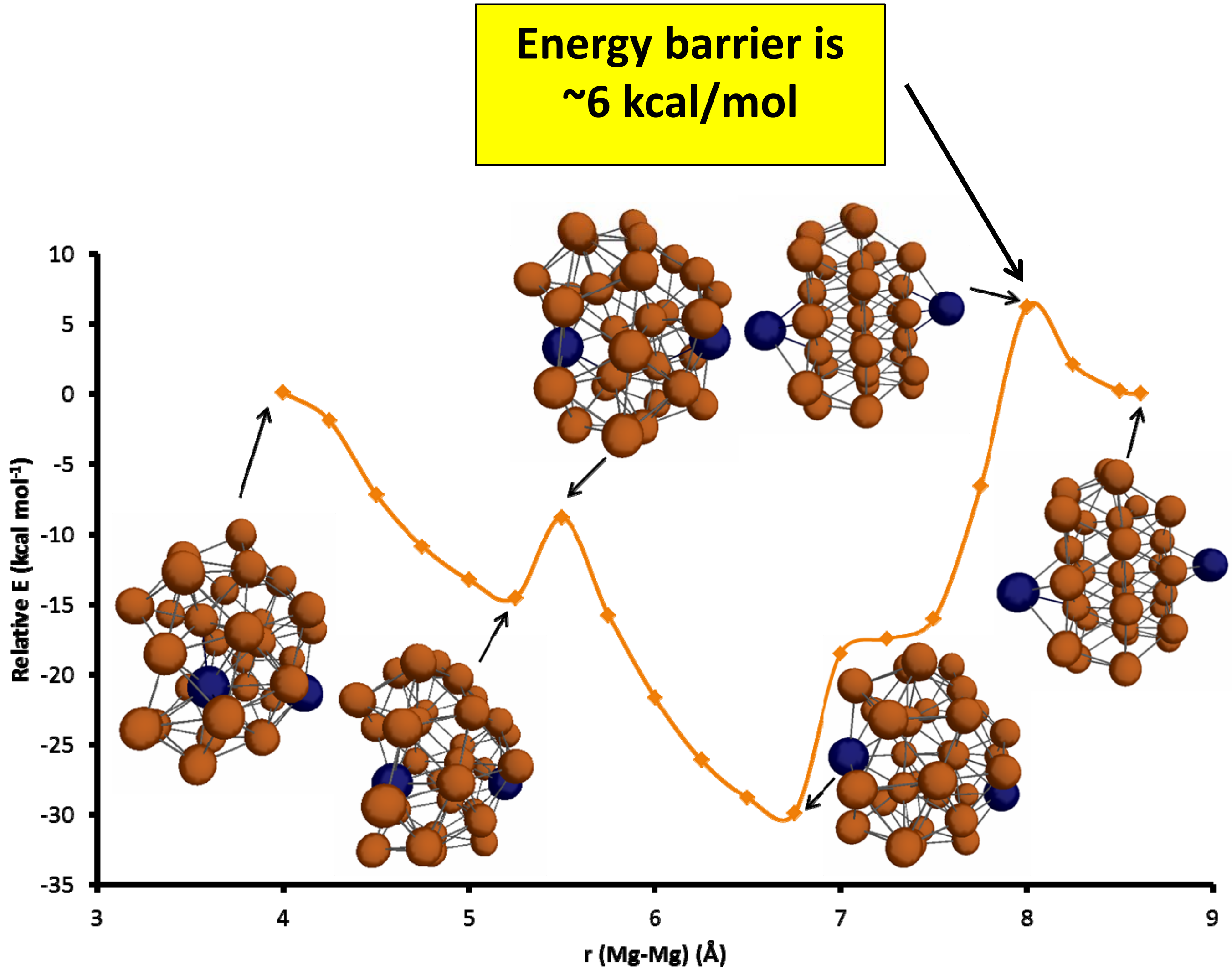
DFT calculations: B3PW91/aug-cc-pωCVTZ(-PP) level

Cu_2Mg_{30} vs. Mg_{30}

Drop in energy in Cu_2Mg_{30} is <u>not</u> due to Mg_{30} rearranging to more stable structure.



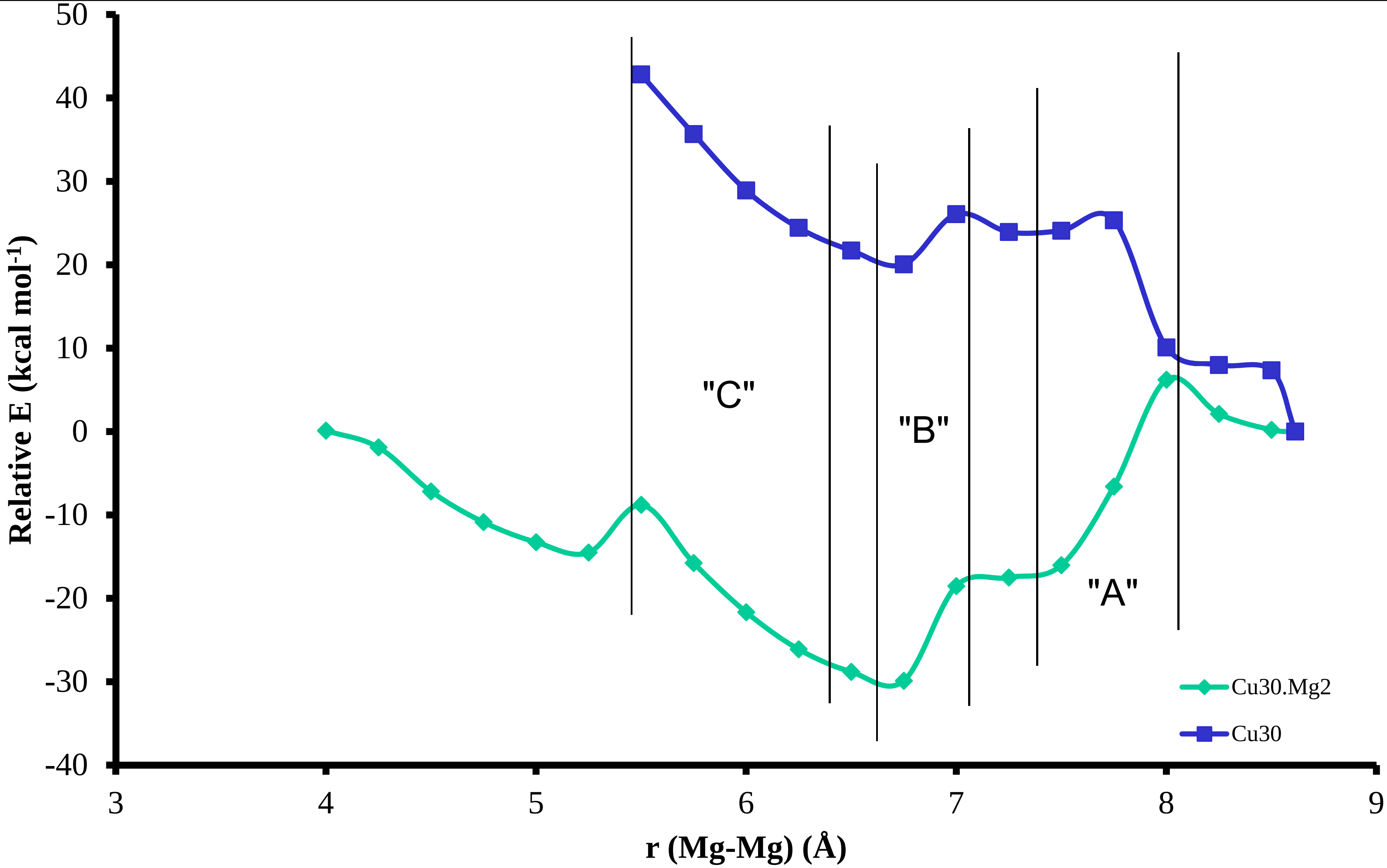
$Cu_{30}Mg_2$



Energy barrier is ~6 kcal/mol
Relative E (kcal mol⁻¹)
r (Mg-Mg) (Å)
10
5
0
-5
-10
-15
-20
-25
-30
-35
3
4
5
6
7
8
9

Mg_2Cu_{30} vs. Cu_{30}

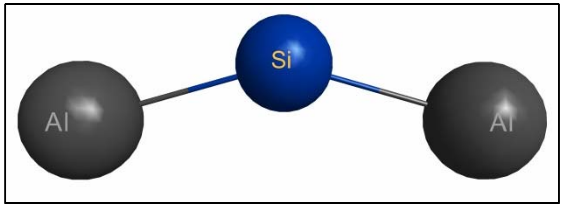
Drop in energy in Mg_2Cu_{30} is not due to Cu_{30} rearranging to more stable structure.



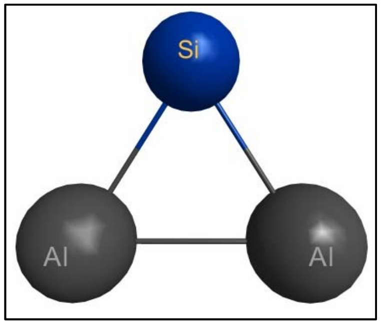
Formation of $SiAl_2$

MRMP2(10e,12o)/aug-cc-pvtz level of theory

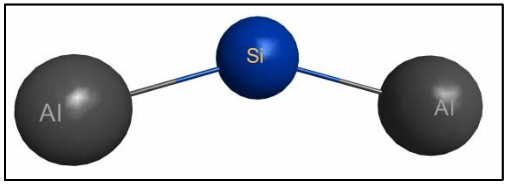
Cyclic isomers



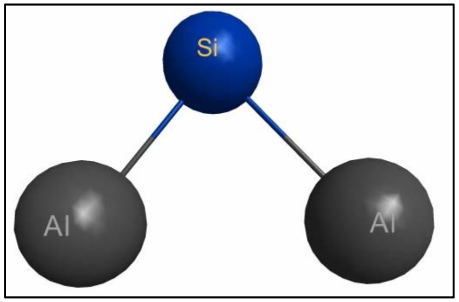
$^5A_1$, -0.63 eV



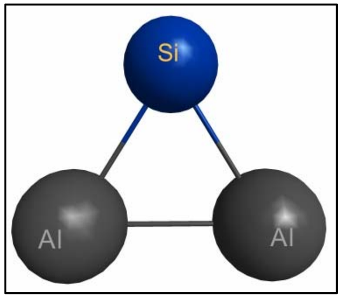
$^5A_2$, -1.55 eV



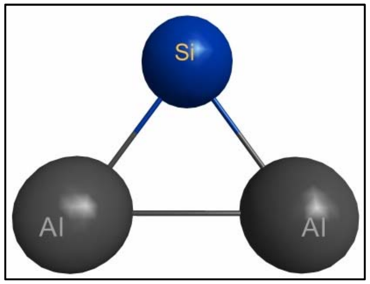
$^3B_1$, -1.59 eV



$^3A''$, -1.80 eV



$^1A_1$, -2.00 eV

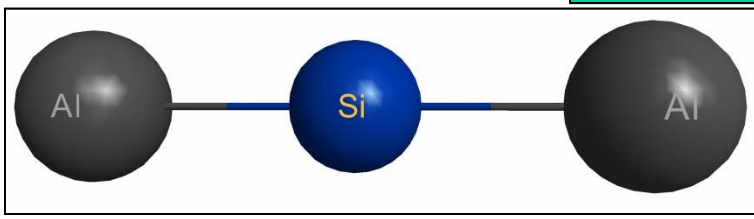


$^3B_2$, -2.04 eV

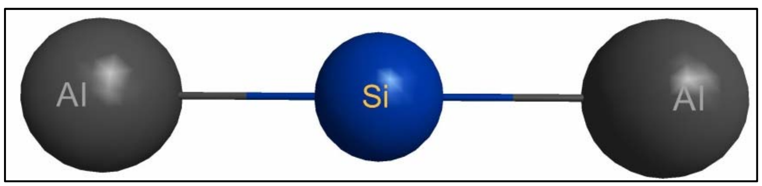
Formation of $SiAl_2$

MRMP2(10e,12o)/aug-cc-pvtz level of theory

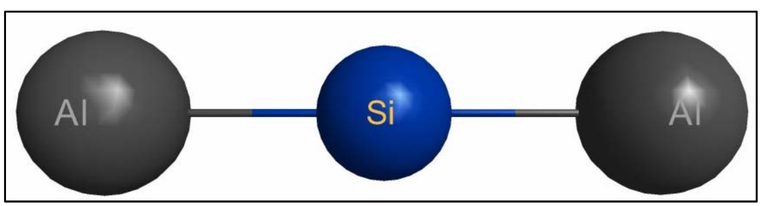
Linear isomers



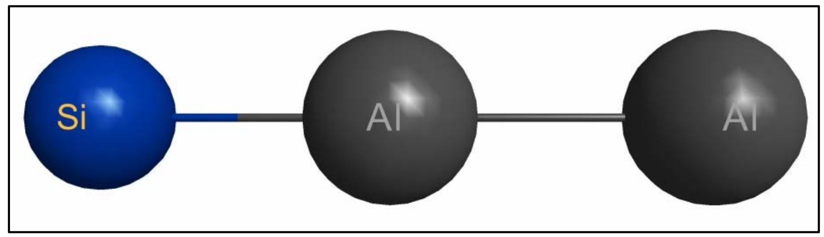
$^5\Pi_u$, -0.58 eV



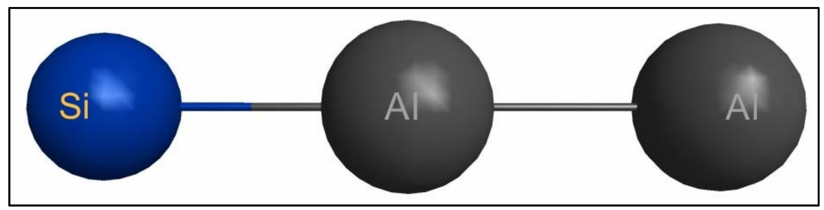
$^1\Sigma_g^+$, -0.89 eV



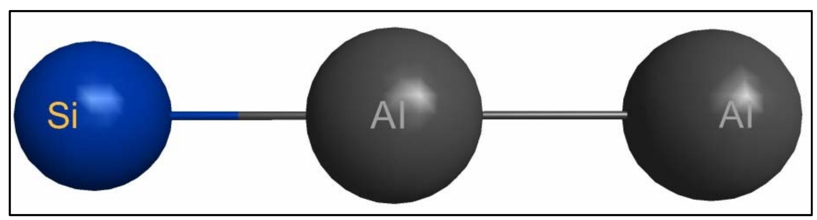
$^1\Pi_u$, -1.28 eV



$^1\Pi$, -0.64 eV



$^5\Pi$, -0.70 eV



$^3\Pi$, -0.94 eV

Summary and Conclusions

- **Mg/Cu core-shell nanoclusters**
  - Helium droplet experiments show inversion of Cu_xMg_y clusters to Mg_yCu_x.
  - Cu atoms diffusing into $Mg_{30,}$ and vice-versa, have been modeled using DFT.
    - Estimated barrier for Cu atoms to migrate into Mg_n is < 1 kcal/mol.
    - Estimated barrier for Mg atoms to migrate into Cu_n is 6 kcal/mol.
  - Calculations are consistent with observed Cu/Mg inversion.

- **$SiAl_n$ clusters**
  - $SiAl_2$ has multiple local minima which are more stable than ground state SiAl ($^4\Sigma^-$) + Al (^2P)
    - Cyclic (C_{2v} and C_s) and linear ($D_{\infty h}$ and $C_{\infty v}$)
    - Singlet, triplet, quintet states
  - At long SiAl--------Al separations, preferred approach is linear
    - Al-Si-Al: $^5\Pi_u$ can form without a barrier
    - Si-Al-Al: $^5\Pi$ can form without a barrier
  - Barriers for linear ↔ cyclic isomerizations TBD
  - In helium droplet environment, linear quintet states may be formed.

Acknowledgements

Core-shell nanoparticles

- Dr. Robert Buszek (ERC, Inc.)
- Dr. Sam Emery(NSWC-IH), Y. Xin (Florida State Univ.),
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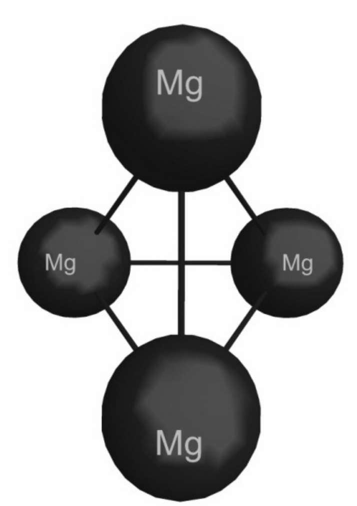
AFOSR

Dr. Mike Berman

DoD HPCMP

Backup Slides

Mg_n benchmark calculations



Mg_n clusters

"Closed shell" atomic configuration $[(1s)^2(2s)^2(2p)^6(3s)^2]$ suggests that weak dispersion interactions will be important. Need to consider

- core-core and core-valence correlation
- correlation method (MP2, CC, DFT)
  - "active" electrons to be correlated in MP2, CC
  - suitable DFT functional for larger Mg_n clusters (up to $n \approx 100$)

Method	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ
MP2	23.1 / 3.042	28.5 / 3.013	29.1 / 3.011
CCSD(T)	16.7 / 3.100	tbd / 3.064	tbd / 3.065
DFT/B3PW91	26.5 / 3.092	26.5 / 3.091	26.4 / 3.092
DFT/PBE	34.6 / 3.070	34.5 / 3.070	34.3 / 3.070
DFT/PBE0	31.5 / 3.078	31.5 / 3.078	31.4 / 3.078
DFT/M06	30.8 / 3.028	30.4 / 3.025	TBD / TBD
DFT/M11	19.2 / 3.134	TBD / TBD	TBD / TBD

Calculated binding energies used to determine size of helium droplet needed for evaporative cooling

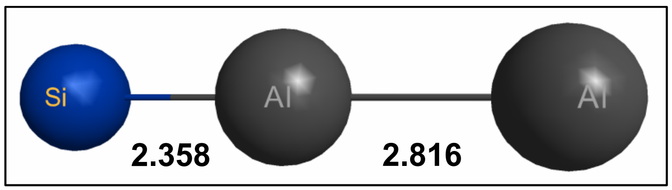
$SiAl_n$

Calculate potential energy surfaces of stepwise atomic addition reactions; e.g., $SiAl_n + Al \rightarrow SiAl_{n+1}$

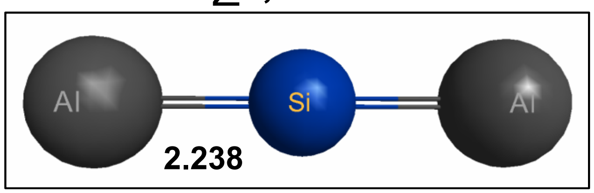
Diatomic: Si (^3P) + Al (^2P) → SiAl ($^4\Sigma^-$)

Triatomic: SiAl ($^4\Sigma^-$) + Al (^2P) → $SiAl_2$ (triplet or quintet)

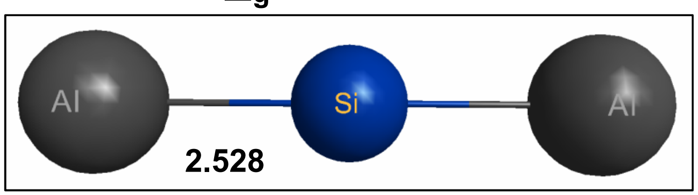
ZAPT(2)/aug-cc-pvtz level of theory



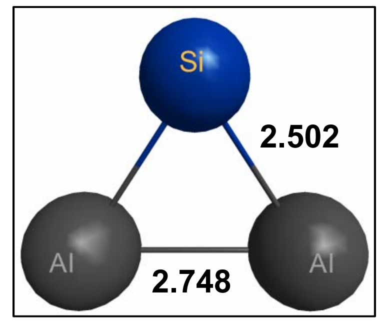
$^3\Sigma^-$, -1.28 eV



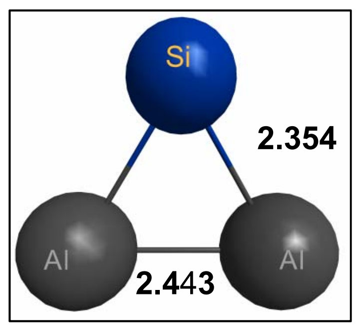
$^1\Sigma_g^+$, -1.70 eV



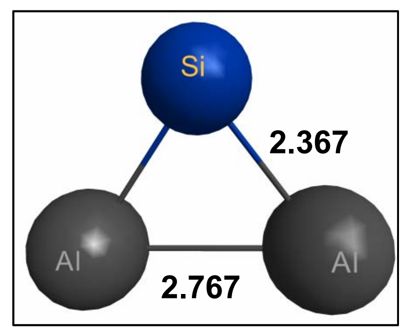
$^3\Sigma_g^-$, -1.93 eV



$^5A_2$, -1.77 eV



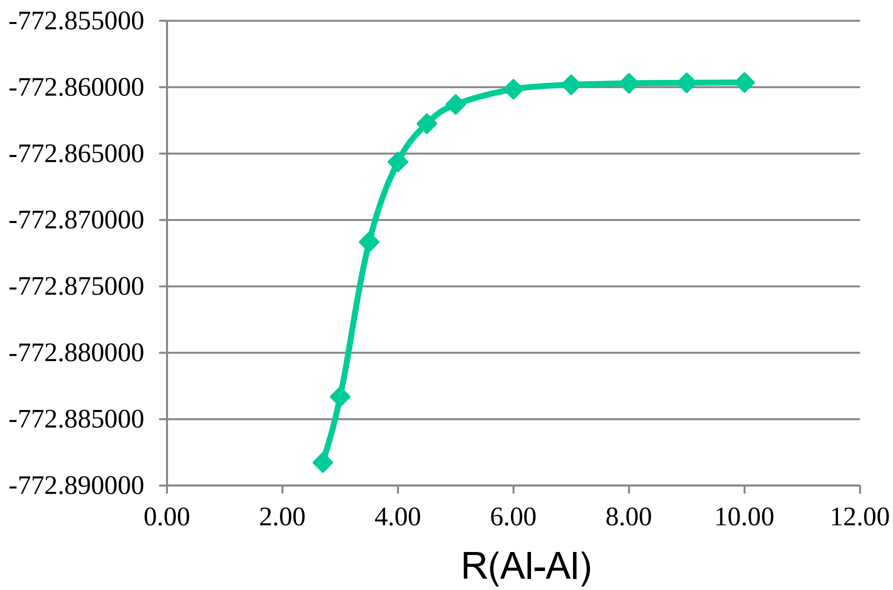
$^1A_1$, -2.65 eV

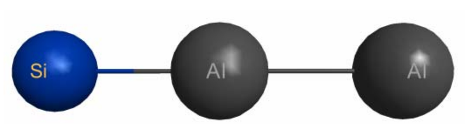


$^3B_2$, -2.67 eV

$SiAl + Al \rightarrow SiAl_2$

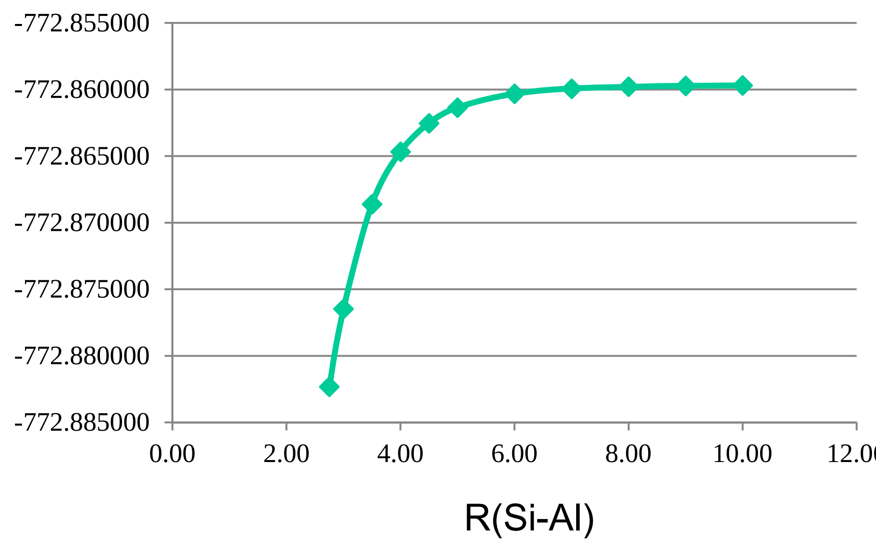
$SiAl\ (^4\Sigma) + Al\ (^2P)$

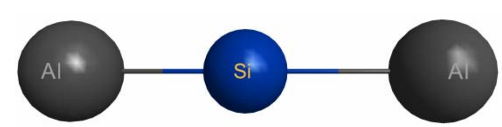




$(^5\Pi)$

$AlSi\ (^4\Sigma) + Al\ (^2P)$





$(^5\Pi)$

MRMP2(4e,5o)/aug-cc-pVTZ